Figure 17

EFFECT OF RELAXATION OF FREEZE/FLASH POINTS ON MAXIMUM THEORETICAL YIELD OF JP-5 CRUDE J, MEDIUM, SWEET, NIGERIAN CRUDE

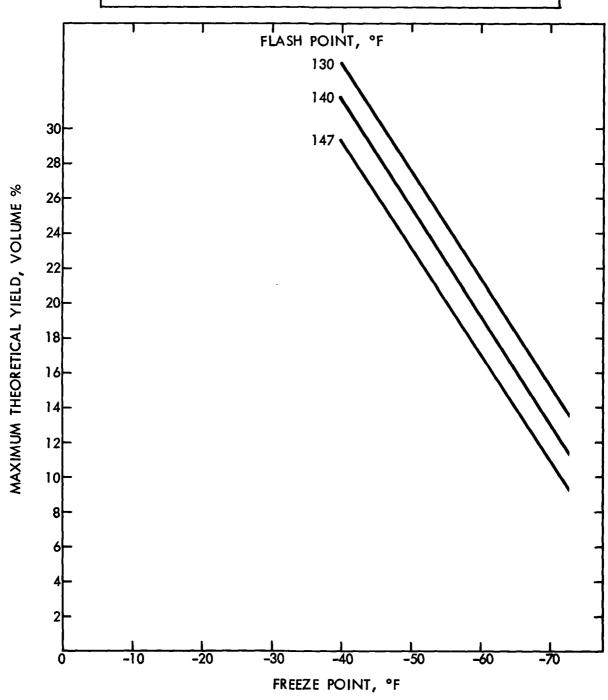


Figure 18

EFFECT OF RELAXATION OF FREEZE/FLASH POINTS ON MAXIMUM THEORETICAL YIELD OF JP-5 CRUDE K, LIGHT, SWEET ABU DHABI CRUDE

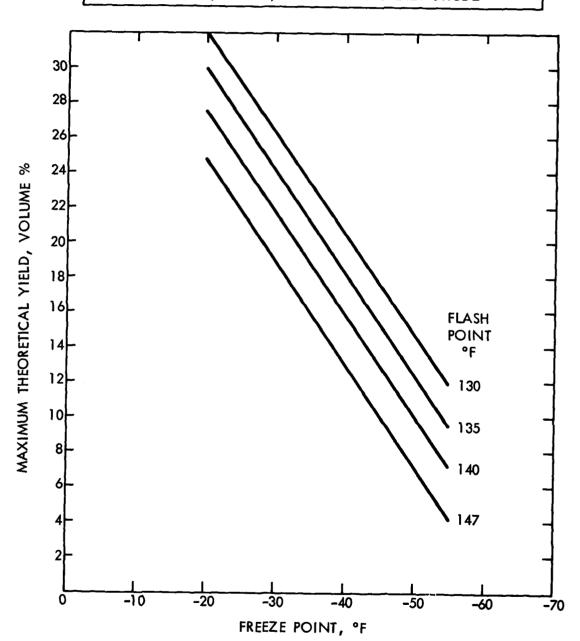


Figure 19

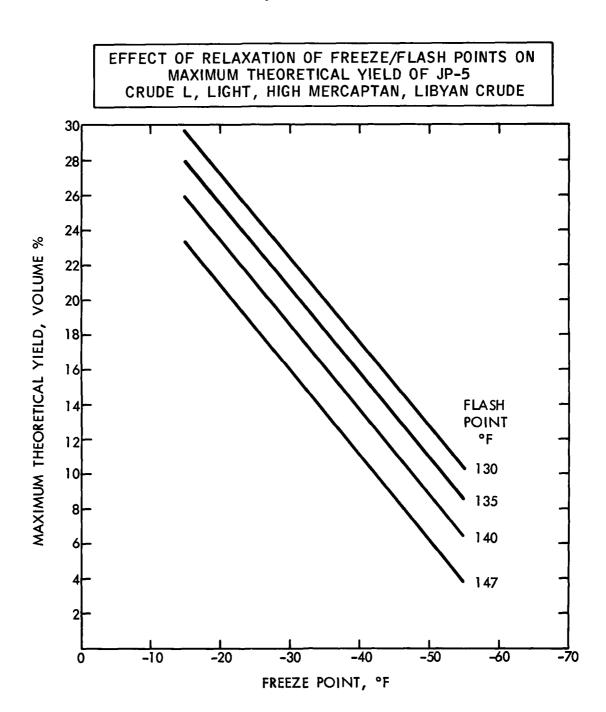
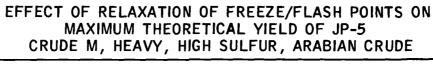
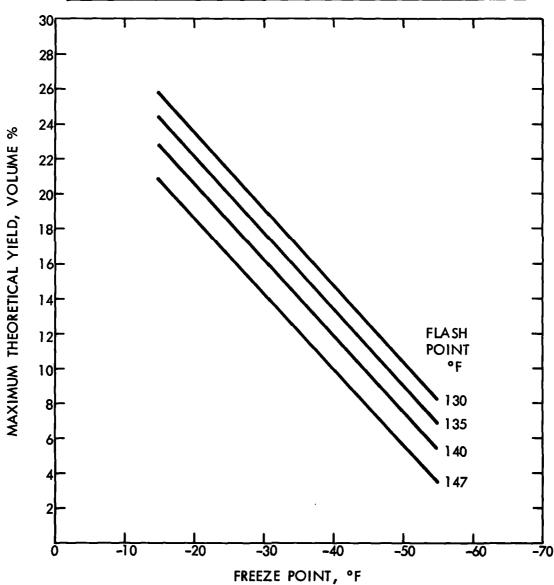


Figure 20







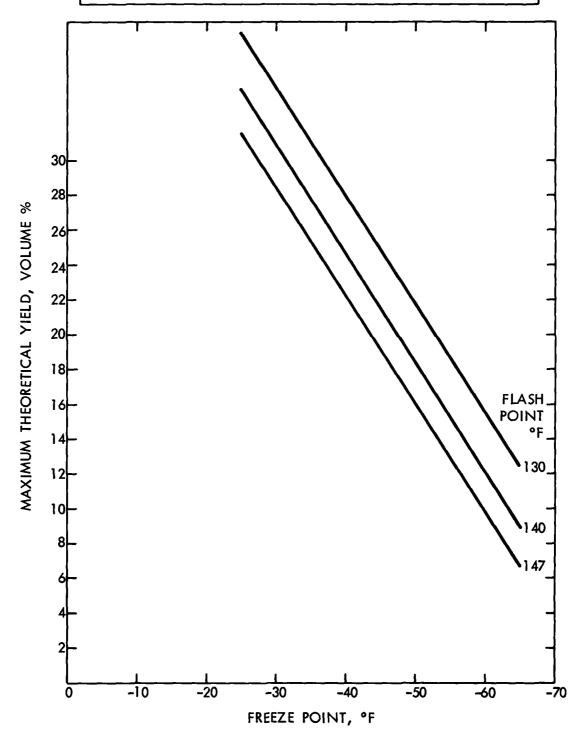


Figure 22

EFFECT OF RELAXATION OF FREEZE/FLASH POINTS ON MAXIMUM THEORETICAL YIELD OF JP-5 CRUDE O, WESTERN TEXAS MEDIUM, SOUR CRUDE

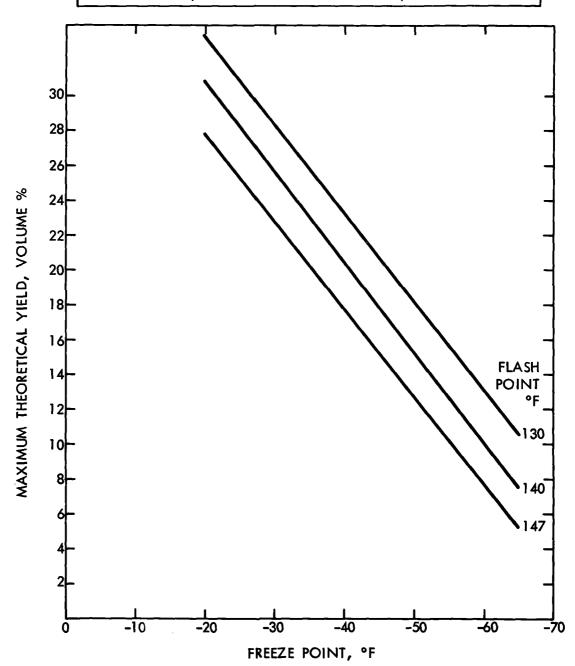


Figure 23

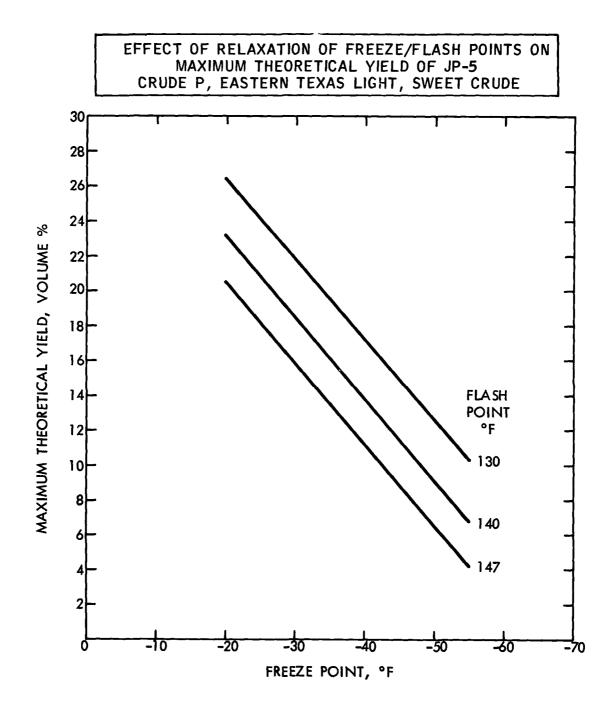
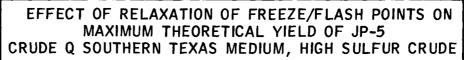


Figure 24



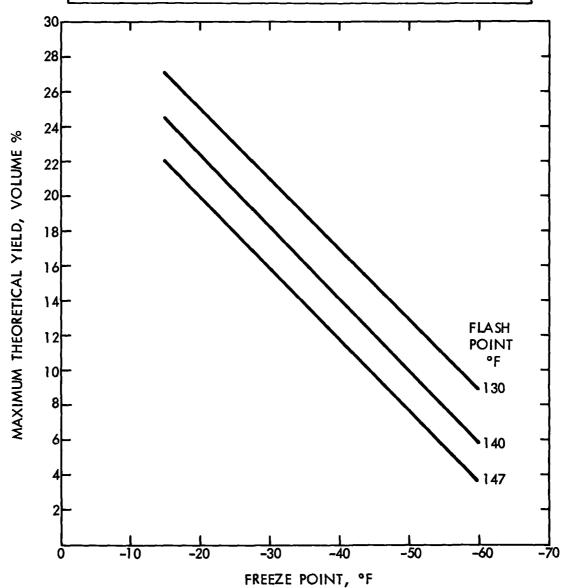


Figure 25

EFFECT OF RELAXATION OF FREEZE/FLASH POINTS ON MAXIMUM THEORETICAL YIELD OF JP-5 CRUDE R, HEAVY, VERY SOUR TEXAS CRUDE

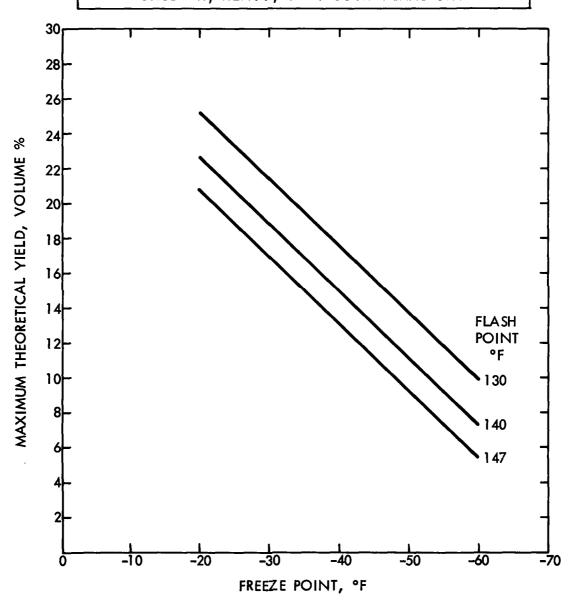
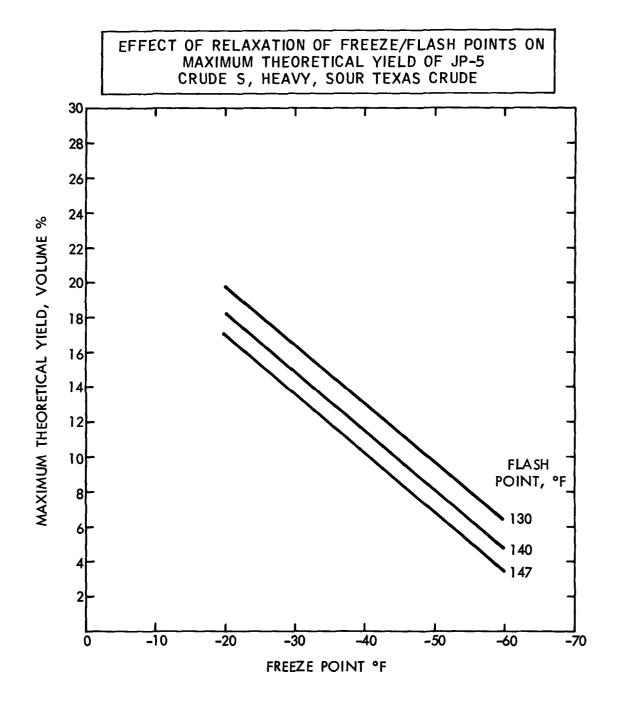


Figure 26



# 4.3 JP-5 Property/Yield Trade-Off Studies for the Strategic Petroleum Reserve (SPR)

The Strategic Petroleum Reserve (SPR) discussed in Task 1 represents a potential source of crudes for the production of military fuels including JP-5 in emergency situations such as crude embargoes. Thus, it is useful to investigate the properties of JP-5 that could be derived from SPR blends. This was done with Exxon's ASP Program using estimates of the current composition of crudes in the SPR and assuming complete mixing of these crudes for the two storage facilities available.

Table 27 gives the gravity, API, pour point OF and total sulfur, wt % of each of the major crudes present in the current Strategic Petroleum Reserve blends identifed here as Blends 1 and 2, respectively. Basically, the SPR crudes are segregated according to gravity and sulfur content; Blend 1 contains medium gravity (28-34) high sulfur content (> 1.0%) crudes, whereas Blend 2 contains relatively light, low sulfur crudes.

Table 28 gives the results on the Maximum Theoretical Yields potentially derivable from these SPR blends and the properties of the distillates to be made into JP-5. Yields are seen to be comparable to those derived from medium and light gravity crudes reported in the preceding pages.

The JP-5 distillate derived from distillation of Blends 1 and 2 is seen to pass most of the JP-5 inspections except for the mercaptans level which exceeds the JP-5 Military Specification in the case of Blend 2 only. The distillate derived from Blend 2 would thus require further processing (e.g. HYDROFINING, sweetening) to reduce the mercaptans below the upper limit of 10 ppm.

 Effect of Relaxation of Freeze and/or Flash Point on Maximum Theoretical Yields of JP-5

The effect of relaxation of the Freeze and/or Flash point of JP-5 fuel on its potential availability from both SPR crude blends was examined using the Exxon Assay Stream Program. The results are summarized in Tables 29 and 30 and Figures 27 and 28.

Significant potential increases in JP-5 yield from both SPR blends are possible from relaxation of either Freeze or Flash Points. Increasing the acceptable Freeze Point levels to  $-45^{0}\mathrm{F}$  gives a 32-35% increase in MTY. As much as a 60-65% increase is potentially attainable with an increase to  $-40^{0}\mathrm{F}$  and increases exceeding 100% are possible at  $-30^{0}\mathrm{F}$ . Similarly, relaxation of the Flash Point to I350F could potentially increase yields over current specifications 17-20% and 38-40% at  $130^{0}\mathrm{F}$ . Yield/Freeze Point and Yield/Flash Point coefficients are generally comparable to the data presented on individual crudes.

TABLE 27

PROPERTIES OF CRUDES BEING STORED IN THE STRATEGIC PETROLEUM RESERVE

	Stra	ategic Pet	roleum Re	serve Bl	end
Property	Blend 1	SPR-A	SPR-B	SPR-C	SPR-D
Gravity, API		32.8	33.9	33.4	28.8
	Blend 2	SPR-E	SPR-F	SPR-G	
		37.6	36.7	40.4	
Pour Point <sup>O</sup> F	Blend l	SPR-A	SPR-B	SPR-C	SPR-D
		-40	5	-30	20
	Blend 2	SPR-E	SPR-F	SPR-G	
	{	10	25	30	
Total Sulfur, wt%	Blend 1	SPR-A	SPR-B	SPR-C	SPR-D
,		1.6	1.4	1.8	1.0
	Blend 2	SPR-E	SPR-F	SPR-G	
		0.20	0.33	0.21	

TABLE 28

PROPERTIES AND MAXIMUM THEORETICAL YIELD (MTY)

OF JP-5 DERIVABLE FROM THE

STRATEGIC PETROLEUM RESERVE (SPR)

	SPR Crude	de Bl <b>en</b> d	
Property	Blend 1	Blend 2	
Flash Point <sup>O</sup> F	140	140	
Freeze Point <sup>O</sup> F	-51	-51	
Gravity, API	45	44	
Aromatics, Vol.%	20.2	16.5	
Smoke Point	23.0	22.4	
Total Sulfur wt%	0.14	0.026	
Mercaptan Sulfur, ppm	6.6	41.1	
Maximum Theoretical Yield (MTY) Vol.%	8.2	9.4	

TABLE 29

EFFECT OF RELAXATION OF FREEZE POINT ON MAXIMUM THEORETICAL YIELD OF JP-5

	Maximum Theor	etical Yield(1)
Freeze Point <sup>O</sup> F	SPR Blend 1	SPR Blend 2
-51 (Current Specification)	8.2	9.4
-45 % Increase Over Current Specification	11.1 35%	12.4 32%
-40 % Increase Over Current Specification	13.5 65%	15.0 60%
-30 % Increase Over Current Specification	18.4 124%	20.1 114%
Yield/Freeze Point Coefficient, Vol%/OF	0.49	0.51

<sup>(1)</sup> At Constant Flash Point of  $140^{\circ}F$ 

TABLE 30

EFFECT OF RELAXATION OF FLASH POINT ON MAXIMUM THEORETICAL YIELD OF JP-5

	Maximum Theore	etical Yield(1)
Flash Point <sup>O</sup> F	SPR Blend 1	1% SPR Blend 2
<pre>147   % Decrease Under Current Specification</pre>	6.0	6.9 27
140 (Current Specification)	8.2	9.4
135 % Increase Over Current Specification	9.8 20%	11.0 17%
130 % Increase Over Current Specification	11.5 40%	13.0 38%
Yield/Flash Point Coefficient, Vol%/ <sup>O</sup> F	0.32	0.36

<sup>(1)</sup> At Constant Freeze Point of -51°F

Figure 27

EFFECT OF RELAXATION OF FREEZE/FLASH POINTS ON MAXIMUM THEORETICAL YIELD OF JP-5, STRATEGIC PETROLEUM RESERVE BLEND 1

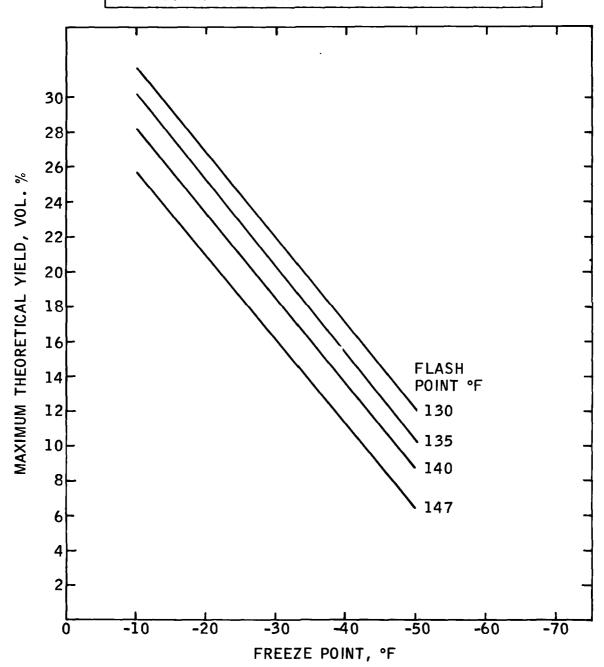
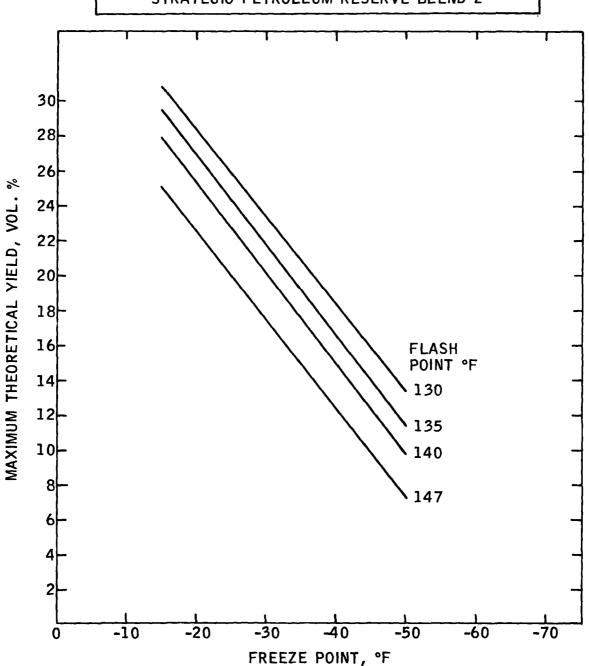


Figure 28

EFFECT OF RELAXATION OF FREEZE/FLASH POINTS ON MAXIMUM THEORETICAL YIELD OF JP-5, STRATEGIC PETROLEUM RESERVE BLEND 2



## 4.4 Summary of JP-5 Property/Yield Tradeoff Studies

The studies conducted on the effect of Freeze and Flash Points on the Maximum Theoretical Yield (MTY) that can be obtained from crudes used widely in PADs 3 and 5, and in the Strategic Petroleum Reserve, have provided useful information on the potential availability of JP-5 from these regions. The more important findings are summarized below.

- The MTY of JP-5 that can be derived from crudes used in PADs 3 and 5 vary widely, i.e. from about 7 to 25 vol. % for current specification fuels.
- The presence of the anti-icing additive ethylene glycol monomethyl ether (EGME) causes a significant reduction in effective volumetric yield because of Flash Point degradation ranging from about 10 up to 40% for the heavier crudes.
- Many of the crudes used in PADs 3 and 5 would require additional downstream processing to remove aromatics and/or mercaptans in order to make acceptable grade JP-5.
- The MTY of JP-5 that can be obtained from the Strategic Petroleum Reserve is about 8-9 vol. %.
- SPR Blend 1 would require no additional downstream processing to make acceptable grade JP-5 and thus could be handled by relatively simple refineries; SPR Blend 2 would require hydrotreating or sweetening to reduce mercaptans to acceptable levels.
- Very significant increases in MTY of JP-5 are potentially possible through relaxation of Freeze and/or Flash Point specifications. Relaxation of Freeze Point generally gives a greater percentage increase in MTY in comparison with the relaxation of Flash Point, i.e. yield/freeze point coefficients generally range from about 0.4-0.6 vol. %/OF and yield/flash point coefficients from 0.2-0.4 vol. %/OF.

## 5. TASKS 5 AND 6 ANALYSIS OF MIDDLE DISTILLATE AND RELATED FUELS

The objective of these tasks is to assess the major trends that are likely to take place, in the near future, in the competitive demand of fuels that are derived from the same, or closely related, distillate fraction of crudes.

The availability of the middle distillate fraction of crudes to make JP-5 will be affected by the competitive demand of other fuels and petrochemical feedstocks which utilize middle distillate or closely associated distillate fractions. Bemands that will compete with JP-5 and thereby could affect its availability include:

- Commercial jet fuels Jet A, Jet B
- Other military jet fuels JP-4, JP-8
- Diesel fuel
- · Distillate heating oil
- Gasoline
- Petrochemical feedstocks

Thus, the extent to which the demand for the above fuels is likely to change in the future could have a major affect on distillate available for JP-5 production.

The approach used in these tasks is qualitative - it would be beyond the scope of this program to attempt to make any quantitative judgments on how future middle distillate and gasoline demand will affect JP-5 availability. However, a qualitative appraisal can be made based on several published fuel demand forecasts. A few of these forecasts are presented in this section. Historical middle distillate consumption trends are presented first.

# 5.1 Review of Historical U.S. Fuel Consumption Patterns

A recent BOM/DOE analysis of refinery yield shows that kerosene jet fuel (commercial jet fuel and JP-5) has represented about 5.5 vol % of the refined product slate (67). This is indicated by the data summarized in Table 31 which show U.S. average refinery yields for the last decade. Total jet fuel yield which includes naphtha JP-4 fuel has been about 6.5-7.0% in recent years after being over 8% during the Vietnam conflict. Gasoline and middle distillates (not including jet fuel) have represented about 43% and 23% respectively, over the years.

An analysis of the users of kerojet fuel indicates that the commercial airlines use about 86% of the total supply, military JP-5 use is about 7% with general aviation and non-aviation use making up the remainder of the total demand. This is indicated by the data shown in Table 32 for 1976 (67).

TABLE 31

REFINERY YIELDS FOR THE UNITED STATES (67)

(Annual Percentage)

	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977 (5)*	1978*	1979*
Gasoline (1)	43.9	44.8	45.3	46.2	46.4	45.8	46.2	46.5	45.6	43.6	43.4	42.2
Total Jet Fuel	8.3	8.2	7.5	7.3	7.1	6.8	6.8	7.0	8.9	6.7	6.7	9.9
Kerosene Jet	5,3	5.7	5.6	5.4	5.4	5.5	5.3	5.6	5.4	5.4	5.5	5.5
Naphtha Jet	3.0	2.5	1.9	1.9	1.7	1.3	1.5	1.4	1.4	1.3	1.2	1.1
Aviation Gasoline	0.8	0.7	0.5	0.4	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.3
Middle Distil- lates (2)	24.8	24.3	24.7	24.0	24.0	24.1	23.0	22.5	22.3	23.5	22.8	22.9
Residual Fuel Oil	7.2	8.9	6.4	9.9	6.7	7.7	8.7	9.9	10.3	11.9	11.9	11.9
Other	18.0	18,3	18.8	18.8	18.6	18.8	18.9	17.5	18.4	17.5	18.4	9.61
Shortages (3)	-3.0	-3.1	-3.2	-3,3	-3.2	-3.6	-3.9	-3.7	-3.7	-3.5	-3,5	-3.5
TOTAL (4)	100.001	100.0	0.00 100.0 100.0 100.0 100.0 100.0 100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Other unfinished oils added to crude oil in computing yields. Includes kerosene.
Processing Gain (-) or Loss (+).
Numbers may not equal total due to rounding.
Revised April 1978 to reflect most recent data.
Projected

SOURCE: U.S. Bureau of Mines and DOE.

TABLE 32
USERS OF KEROJET 1976 (67)

	Thousands of Barrels	Thousands of Barrels Per Day	Percent of Total
Airlines	247,481	678.0	86.0
General Aviation	13,397	36.7	4.7
Aviation Factories	2,220	6.0	0.8
Military	19,648	53.8	6.8
Non-Aviation Use	4,885	13.4	1.7
Total	287,631	787.9	100.0

SOURCE: DOE

Large integrated refiners have historically been the major suppliers of kerojet fuel. This is illustrated in Table 33, which shows that between 1972 and 1975 large integrated refiners produced about 93% of the total kerojet fuel supply (67). However, over the last few years, the role of the small refiners has increased somewhat over that shown.

TABLE 33

REFINER GROUP SHARES OF KEROJET FUEL\_SALES (67)

Year	(000 bbls)*	Large Integrated Refiners	Large Independent Refiners	Small Refiners
1972	228,619	93.5	4.5	2.0
1973	236,929	93.5	4.0	2.6
1974	241,429	92.5	3.5	4.0
1975 (est.)**	250,571	92.5	3.5	4.0

<sup>\*</sup> Excludes bonded fuel imports and direct imports by the DOD and/or other independent marketers.

SOURCE: DOE

<sup>\*\*</sup> Since 1975, refiners reporting to DOE surveys have been instructed to consolidate reports of sales of naphtha jet and kerojet. 1975 estimates of sales are based on DOE kerojet production reports.

# 5.2 Fuel Projections

## • Exxon Fuel Projections

Exxon sees a strong demand for distillates over the near term (through 1984) based on continued economic growth and declining supplies of natural gas (36). Long term average distillate demand growth rate is estimated at about 3.1%/year with demand tapering off about 1990. Factors affecting this growth rate include:

- Conversion of more inter-city freight trucks to diesel fuel.
- Increased dieselization of light-duty trucks and passenger cars.

On the other hand, Exxon projects that motor gasoline will have very slow growth through 1990 when it will account for "less than 30% of total product demand." (It presently represents over 40% of total product demand.) Passenger-car gasoline demand shall grow at about 1%/year and peak in the mid 1980's. This will likely be followed by a decline of about 2%/year through 1990 as a result of:

- Increased fuel efficiency of cars.
- A decline in the annual mileage driven.
- Increase in diesel powered cars.

Exxon sees the demand for heavy fuel oil increasing in the near term as it replaces gas supplies and a reduction in demand after 1985 when the effects of conversion to coal are expected to begin being felt. Exxon's projected petroleum product demand trends in the U.S. are summarized below in Figure 29.

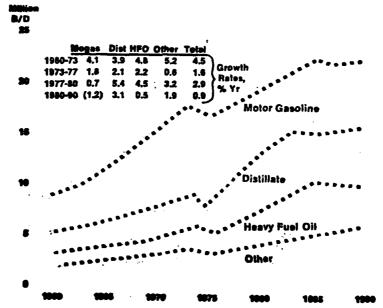


Figure 29. Exxon's Projected United States Petroleum Demand By Product (36)

The increased demand for diesel fuel could have an adverse affect on potential JP-5 availability. This may be somewhat offset by the fact that reduced gasoline consumption may free heavier crude fractions that could now be converted to middle distillate (instead of gasoline) by hydrocracking. The availability of hydrocracking processing capability is relatively limited in the U.S. today, but as indicated in Task 2, should be growing significantly in the U.S. during the next decade.

## Petroleum Industry Research Foundation (PIRF) Projections

The Petroleum Industry Research Foundation (PIRF) generally agrees with the Exxon projections on demand trends for distillates and gasolines though the absolute annual growth rate numbers differ somewhat (37). As shown in Table 34, gasoline demand is expected to peak between 1980 and 1985 and then show a slight decline into 1990. PIRF's 1990 projection for the fractional demand of gasoline is about 30% which agrees closely with the Exxon projection.

Distillates and jet fuel (listed separately in the PIRF projections) show a definite increasing trend through 1990. Residual fuel demand is seen to peak about 1985, then decrease between 1985 and 1990. PIRF sees jet fuel maintaining nearly a 3% annual growth rate through 1990, the largest rate for fuel products.

TABLE 34

PIRF PROJECTION OF U.S. PETROLEUM PRODUCTS DEMAND, 1965-1990(37)
(MILLION BARRELS DAILY)

	1965	1973	1976	1900	1005	3990
Complines (1). Distillates (2). Residual fuel oil. Just fuel. Other.	4.71 2.13 1.61 0.60 2.25	6.72 3.09 2.82 1.06 3.61	7.02 8.13 2.79 0.99 3.51	7.48 3.55 3.50 1.11 4.29	7.24 3.89 3.67 1.27 5.04	7.00 4.13 3.32 1.48 5.66
Tetal	11.30	17.30	17.44	20.02	21.11	21.65

# Average Annual Growth Rate (% per year)

	1965/73	1973/76	1976/80	1960/85	1985/90	1976/90
Gesolines. Distrilates Residual tuel oil. Age fuel Other	7.3 7.4	1.5 0.4 -0.3 -2.2 -0.7	1.6 3.2 6.5 2.9 5.1	-0.7 1.9 0.4 2.7 3.3	-0.7 1.2 -1.7 3.1 2.4	8.0 2.0 1.4 2.9 3.5
Total	5.2	0.3	3.5	LI	0.5	1.6

(1) Includes aviation gasoline.
(2) Excludes aetrochemical foedstock use of gasail which is included in "Other"

Within the distillate fuel oil sector, PIRF sees the residential/commercial demand increasing at a modest rate (< 2% annually) to about 1980, stabilizing in the mid 1980's, then declining at a very modest rate until 1990. Reduction in demand is seen to reflect increased energy conservation measures, particularly improvements in the insulation of residential structures.

In contrast to developments in the residential market, PIRF sees distillate fuel oil demand in the industrial market rising rapidly over the next 4-5 years because of declining natural gas supplies. However, increased use of coal is seen as ultimately causing a leveling off of distillates demand. The major growth in distillate fuel from 1985 to 1990, PIRF believes, will come primarily from its use as an automotive passenger car fuel (i.e. diesel fuel).

Jet fuel demand, according to PIRF, will grow at about twice the rate of total petroleum products. They see U.S. commercial aviation expansion being very dependent on jet fuel availability for the next 14 years.

In making the above estimates, PIRF assumed a GNP growth of 4% per year through 1980 and then a 3.2% growth rate until 1990. Since overall energy demand growth is closely tied to the growth in GNP (  $\sim$ .71% in energy demand/% GNP according to PIRF) their projections are contingent on the performance of the economy.

## • Pace Co. Fuel Projections

Pace Co., a Houston based consulting firm, also predicts that the fuel demand trend will shift toward greater consumption of distillates with a corresponding decrease in gasoline consumption. Their predictions are illustrated graphically in Figure 30.(25).

Based on the presented fuel projections, the following conclusions can be drawn:

- Supplies of jet fuel including JP-5 will probably become increasingly tight. This will be primarily due to an increased demand for middle distillates, primarily diesel fuel.
- The rapid increase projected for commercial jet fuel demand should also provide additional pressure on supplies of JP-5.
- Conversion technology, particularly hydrocracking, may be an attractive way of increasing middle distillate supplies. Since there is likely to be a reduction in gasoline demand during the next decade, crude stocks previously used for gasoline production (through catalytic cracking) could be made available for middle distillate production.

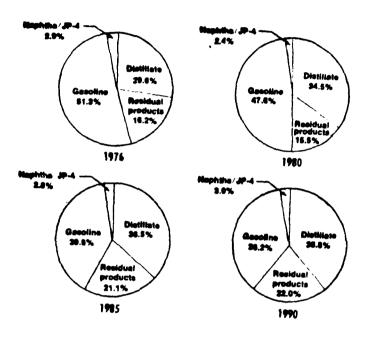


Figure 30 Pace Co. Predicted Trends in U.S. Refinery Product Yields (25)

## 5.3 Potential Effect of Deregulation of Kerosine Jet Fuel

#### • 01d JP-5 Procurement Process

JP-5 production in the U.S. has been controlled by the 1974 Petroleum Allocation Law which fixed both the price and source of supply between 1974 and early 1979 when the law expired. Refineries that were supplying JP-5 during the fuel emergency period of 1973-1974 were required to continue to produce the fuel in an amount proportional to their 1973-1974 base period contribution. The price of the fuel was also regulated by law.

In contrast to the domestic procurement of JP-5, JP-5 produced overseas is procured entirely in an open competitive bid process. Assuming technical capability is assured, this award is made on minimum price to the government. This implies that the overseas refinery mix making JP-5 could vary considerably more than that for domestic JP-5. In practice, however, refinery location and logistics narrows the choices considerably and the foreign refinery mix also stays relatively constant.

## • Deregulation of JP-5

The law governing the control of kerosine jet fuel prices and mandatory allocations expired February 1979. This event may have an important effect on the availability of JP-5 produced in the U.S.

The result of the above law was to keep the refinery suppliers in the U.S. that provided JP-5 virtually the same over the last 5 years. Refiners were required by law to provide JP-5 at a fixed price. (Some small variation did exist as a few contracts were solicited on a competitive basis to ensure that an adequate supply of JP-5 was made available. The additional, non-mandatory, portion, usually amounted to about 5-10% of the JP-5 made.)

Now that the mandatory allocation of kerosine jet fuel has been removed, it will be important to see if the refinery mix that will provide JP-5 to the U.S. Navy will change substantially. Since prices will be allowed to rise somewhat, there may be more refineries interested in participating in bidding for JP-5 contracts. On the other hand, some of the administrative problems that are associated with implementing contracts may dissuade some of those, who previously participated, from continued involvement.

Based on a preliminary review of the responses to JP-5 procurements in 1979, it appears that there has been little change in the composition of the refinery mix producing JP-5 as a result of deregulation. Virtually, all of the refiners previously providing JP-5 under the allocation act have continued to make JP-5 available to the Navy.

# 6. TASKS 7 & 8 NAVY ENGINE/AIRFRAME/FUEL STORAGE AND TRANSPORT/FUEL SENSITIVITY ANALYSIS

The objective of this task is to review and analyze specific problems associated with using JP-5 in aircraft. Case histories of the major operational problems that have recently occurred are analyzed and discussed. In addition, problems with the future operation of JP-5, as identified in the Task 9 matrix analyses are also identified and discussed below.

To date, there have been two major problem areas associated with the use of JP-5 in engines. These are both related in that the primary reasons for their occurrence are linked to the type of processing scheme employed to make the fuel. The two major problem areas are:

- Fuel peroxidation and the subsequent attack by this fuel on elastomeric materials, specifically neoprene gaskets.
- Production of fuel with apparently poorer lubricity characteristics.

In connection with the second, a related problem of fuel filter plugging developed which was a result of a specific remedy employed to solve the lubricity problem. These problems are each discussed, in turn, below.

#### • The Occurrence of Organic Peroxides in JP-5

A detailed analysis of the buildup of peroxide in JP-5 and its consequences has been made by Shertzer(95). In reviewing the development of the problem, this report indicates that problems began to develop in the spring of 1976, when the Navy experienced a number of compressor stalls in A-7E aircraft operating from the U.S.S. Ranger (CV-61) while deployed in the Western Pacific (WESPAC) area. The condition resulted in the loss of one A-7E aircraft. The results of a detailed investigation which included representatives from the Navy, Air Force and several U.S. companies, indicated that the presence of peroxides in WESPAC JP-5 fuel was responsible for the failure of a neoprene diaphragm in the hydro-mechanical governor (HMG) located in the high pressure fuel pump used in the TF 41-A-2 engine. The HMG failure prevented the compresssor inlet guide vanes from operating, resulting in the stall conditions.

Subsequent investigative work performed by the Navy, and Lucas Aerospace, Ltd. of the United Kingdom (manufacturer of the pump) verified that:

- peroxides were present in the JP-5 fuel involved in the aircraft incidents;
- peroxides can detrimentally affect the life of the neoprene diaphragm used in the HMG;

 failure of the neoprene diaphragm will cause the engine to incur a compressor stall condition.

It was suggested (though no definite evidence for it was presented) that other elastomers (other than neoprene) may also have been detrimentally affected by the JP-5 fuel containing high peroxide concentrations.

As a result of the above, the following action was taken in the field:

- (1) JP-5 stocks had to be segregated to insure that A-7E aircraft received only JP-5 containing no (or low) concentrations of peroxides.
- (2) Peroxide levels of JP-5 had to be frequently determined in the field using a laboratory technique not considered satisfactory for field use.

The report concludes that:

- Removal of the formed peroxides by clay filtration did not appear to provide a satisfactory solution -- regeneration of peroxides took place after treatment.
- The use of two specific oxidation inhibitors, approved for use under MIL-T-5624, prevented significant fuel peroxidation.
- The most abundant peroxides present in the contaminated fuel appeared to be secondary hydroperoxides of aromatic hydrocarbons having the general formula  $CnH_{2n-8}$ ,  $CnH_{2n-10}$ .
- The principal cause of the peroxide formation problem was believed to be related to the hydrogen treatment process used in the refining of the JP-5 of concern.

The failure of other rubber components in aircraft fuel systems due to peroxides in the fuel have been reported previously (to the Navy protiems) by several commercial airways. Both nitrile rubber and neoprene have developed cracks due to peroxides in the fuel.

Examination of several batches of jet fuel that had been hydrotreated (in connection with similar problems experienced by commercial airlines) indicated that several of the fuel batches which developed peroxides were hydrotreated. Fuels which had not received hydrogen treatment did not develop peroxides. Apparently, the specific conditions of the hydrotreating process involved (temperature, pressure, catalyst, space velocity) are important in determining whether the fuel will have a tendency to form peroxides during storage. The use of anti-oxidants was found not to correct the trouble if peroxides had already been formed before addition.

It has been known for some time in the petroleum industry that severe hydrofining can remove natural inhibitors present in crudes. It has thus been general practice to add anti-oxidants to hydrofined streams. (This is not always done, especially if their hydrofined component is subsequently blended with other streams still containing natural inhibitors).

There is an increasing trend in the use of hydrotreating to desulfurize fuel in jet fuel production and thus the potential for more peroxide buildup could increase. This is particularly the case in PAD 5, where more and more Alaskan North Slope crude is being used to make JP-5. This crude is particularly high in aromatics content and thus more severe hydrotreatment may be used in the future to meet smoke point and/or aromatics content specifications. The use of anti-oxidant additives in all JP-5 produced should, however, prevent further problems associated with peroxide buildup.

The latest version of the JP-5 military specification (MIL-T-5624L) makes use of anti-oxidants mandatory in all fuels delivered without regard for the type of processing employed. This should help in preventing the formation of deposits through peroxidation. But these areas should be watched very closely.

Improved quality control of JP-5 with regard to the peroxidation problem may be possible by reduction of the allowable types of anti-oxidants that may be used in JP-5. The current number of approved formulations are many. A recommendation is made by Shertzer(95) in which a program to evaluate the relative performance of all currently approved oxidation inhibitors is suggested.

## • Problems Related To Fuel Lubricity Properties

Apparent problems which were related to JP-5 fuel lubricity were experienced by the Navy in the mid-1979's with A-7B aircraft operating in the Mediterranean. These aircraft experience problems with fuel control valves which were attributed to the use of low lubricity fuel. Subsequent to this, failures of F-14-A afterburner hydraulic fuel pumps were also traced to the use of low lubricity fuels(96).

It is generally accepted by Navy personnel that JP-5, produced using severe hydrotreatment (e.g. hydrocracking) in the processing, yields a fuel with lubricity characteristics that can adversely interact with certain specific fuel system components. This is believed to be caused by the removal of naturally occurring impurities such as organic acids and some polynuclear hydrocarbons which impart good lubricity.

The approach chosen by Navy personnel to deal with this problem is to call for the use of an approved corrosion inhibitor in all JP-5 produced, regardless of the type of processing employed. This has become formally effective in MIL-T-5624L.

The above solution to the lubricity problem associated with some hydrotreated JP-5 has some potential pitfalls. Firstly, the use of corrosion inhibitors(dibasic acid formulations) increases the tendency of the JP-5 to retain water through emulsions. This is reflected in the downgrading of the WSIM specification from 85 to 70. Increased emulsion formation results in

the accumulation of more scale in the fuel which can increase fuel filter plugging. With the use of the corrosion inhibitor formulations, there is an increased tendency to pick up scale from previously corroded brass pipes and from storage tanks. Increased copper oxide scale in the fuel could possibly lead to enhanced fuel deposit formation as dissolved copper is capable of catalyzing fuel decomposition. Increased fuel water content may lead to the corrosion of some fuel system parts which in turn could contribute to lubricity problems resulting from metal wear. Also, increased retention of water in the fuel as a result of emulsion formation can lead to more rapid deactivation of fuel filter coalescers.

Alternate solutions should be considered such as replacement or modification of specific hardware involved (since the problem is limited to certain engine/aircraft components). Further, it may be useful to determine at what point severe hydrotreatment (i.e. which conditions, composition, pressure, catalyst, hydrogen partial pressure) is likely to adversely affect the lubricity of the final jet fuel produced.

## • Fuel Filter Plugging Problem

Closely connected with the above is an actual field problem experienced aboard the U.S.S. John F. Kennedy (CV-67). JP-5 fuel contamination caused complete blockage of the 100 mesh screens in the refueling nozzles at the fueling stations. This rendered aircraft refueling impossible.

An analysis of the problem by Navy personnel identified the probable cause as a lifting of scale formed in the piping and storage vessels of the JP-5. The scale was apparently lifted into the JP-5 after a specific corrosion inhibitor was injected into the fuel on-board the ship. The corrosion inhibitor was being used to improve the lubricity of the fuel as discussed above. The scale was believed to be lifted as a result of overtreatment or poor control of the concentration of corrosion inhibitor employed. The scale was experimentally characterized as being primarily oxides, hydroxides, carbonates and oxalates of copper.

The contaminated fuel showed indications of impaired thermal stability, which were attributed to small amounts of dissolved copper as suggested in the above discussion of the Navy's current solution to the lubricity problem.

This incident implies that the corrosion inhibitor solution may indeed create other problems in fuel thermal stability and/or handling, and should be evaluated over a period of time. Alternate approaches consisting of modifying specific fuel system hardware components (e.g. a fuel pump or a component in a fuel pump) could ultimately provide a safer and/or more cost effective solution.

### Plugging of Small Filter Screens In A-7 Aircraft

Some recent cases of power failure in A-7 aircraft due to compressor stalls have been attributed to plugging of a small filter screen in the hydromechanical governor (HMG) section of the fuel pump and inlet guide vane control system. The plugging was apparently caused by a gelatinous material present in the fuel which had built up in stagnant areas of the fuel delivery system(98).

X-ray fluorescence analyses of the gel after heating to remove fuel and combustion to remove organic matter showed that high concentrations if silicon were present. The gel was approximately 65% organic and 35% inorganic material; the organic material was found to be aliphatic in nature but did not dissolve in typical aliphatic solvents, indicating a polymeric structure. The mechanism of the gel formation and cause of this problem had not been identified at the time of this writing.

# 7. TASK 9 MATRIX ANALYSIS BY TECHNICAL AREAS - POTENTIAL PROBLEM IDENTIFICATION

This task summarizes the effect of some projected potential changes in JP-5 composition/properties and processing that may have an important impact on fuel technical problem areas including:

- Fuel Storage/Thermal Stability
- Combustion
- Lubricity
- Low Temperature Flow
- Additive Effects

The summary is expressed in the form of matrices which looks at the effect of projected changes in fuel components and/or properties as they relate to several important questions regarding the following:

- How they are affected/controlled by specifications
- How they are influenced by crude oil types, processing and blending
- Fuel storage and handling effects
- Potential effects/interactions with engine components
- Prior incidents or unusual past experiences.

## Matrix Descriptions

The following Matrix Descriptions are used to denote the projected effects on the fuel technical areas of interest.

## Matrix Key Descriptors

- X Has significant effect and/or impact
- 0 Has no significant effect and/or impact
- I Definite increasing trend noted
- PI Has potential for significant increasing trend
- NAT No apparent trend noted

A table of footnotes is associated with each Matrix and provides the supporting text to explain some of the more important projected trends in each of the fuel technical areas of interest.

## 7.1 Fuel Storage/Thermal Stability

Several important classes of compounds have been identified which can have a major impact on JP-5 storage and/or thermal stability. The interaction of these compound classes/additives with the various important aspects of fuel production and handling, engine component interaction, problem incidents, trends in problem severity, coverage by military specification as they relate to fuel storage/thermal stability are summarized in the matrix given in Table 35. Footnote explanations for the Fuel Storage/Thermal Stability Matrix are given in Table 36.

The major points made by the analysis of important trends that can impact on fuel storage and thermal stability include:

- The progressive decrease in crude quality projected into the near future (higher sulfur and aromatics) will require more severe hydroprocessing which may make jet fuels more susceptible to peroxidation as a result of greater removal of natural anti-oxidants present in crudes.
- Increase in the use (or severity) of sweetening processes may result in increased concentrations of disulfide and polysulfide compounds which behave much like peroxide compounds and may make JP-5 (produced using this process) more prone to peroxidation.
- The use of thermally cracked stocks in JP-5 produced in the future may result in the production of a wider range of types of olefins which could, in turn, have a detrimental effect on thermal stability. The proper use of hydrotreatment after thermal cracking, however, should minimize these effects.

#### 7.2 Combustion

The Fuel Combustion Matrix was developed using the fuel component/properties and relevant evaluation criteria listed in Table 37. The interaction of these compounds, and properties with crude, processing, storage and handling, impact on engine/airframe as well as other important criteria related to fuel combustion are also presented. Footnote explanations for the Fuel Combustion Matrix are given in Table 38. The major points made by the Combustion Matrix include:

- The decreasing quality of crudes projected in the future for the preparation of jet fuels including JP-5 are likely to make it more and more difficult to meet fuel Smoke Point and total aromatics specifications. This problem may be handled by more severe hydroprocessing and/or aromatics extraction.
- The formation of soot is greatly dependent on the hydrogen content of the fuel which can be related to the aromatics content and to a lesser extent on the types of aromatic compounds present. The degree of soot formation can affect turbine blade erosion, combustion wall temperature, both of which can greatly affect engine life and maintenance requirements.
- Within the limits of initial and final boiling points for the JP-5 specification, generally only minor differences in volatility distribution will be exhibited by a wide range of crudes. Thus, the decreasing crude quality trend is not likely to affect fuel ignition characteristics, though some minor changes in fuel viscosity may be experienced.

TABLE 35

PROBLEM ANALYSIS MATRIX - FUEL STORAGE/THERMAL STABILITY

		- 110 -	="			
Y es Y es No No No	Yes	0 0 0 0 0 0	Indirectly(1) Indirectly(10) No	Yes No	0 N 0 N	Yes
I 1 PI(8) PI(8) NAT	(7)Iq				NAT PI(9)	(21)Id
X 0 X(13) X(13)	×	000	X(5) X(6)	00	X(14)	( ) X
×o××o	×	000	×××	×o	××	×
coxxo	×	000	×××	00	××	×
××××	(7)X	×××	×××	×o	o× S	( z ) X
××oo×	×	×××	o××	××	00	0
Total Sulfur Mercaptans Disulfides Polysulfides Condensed Thiophenes	Olefins	Total Nitrogen Basic Nitrogen Non-Basic Nitrogen	Peroxides Carboxylic Acids Other Oxygen Compounds	Aromatics n-Paraffins/Naphthenes	Total Dissolved Metals Dissolved Copper	Additives (Anti-Oxidant)
	ur $\begin{array}{cccccccccccccccccccccccccccccccccccc$	ur	es x x x x x x x x x x x x x x x x x x x	X X X X X X X X X X X X X X X X X X X	X X X X X X X X X X X X X X X X X X X	X X X X X X X X X X X X X X X X X X X

#### TABLE 36

#### FOOTNOTE EXPLANATIONS FOR FUEL STORAGE/THERMAL STABILITY MATRIX

- (1) The level of peroxides in JP-5 is controlled indirectly by stability specifications and by the use of anti-oxidant additives after processing by hydrotreatment.
- (2) JP-5 that has been processed by means of hydrotreatment processes are required to have a specified amount of anti-oxidant additives to prevent fuel deposit formation during storage.
- (3) There is no apparent trend (NAT) in the level of total, basic and non-basic nitrogen compounds currently in JP-5. However, any switch to the use of shale oil sources to make JP-5 in the future will cause a marked increase in nitrogen compound levels.
- (4) Though no apparent trend (NAT) is currently discernible in the peroxide buildup in JP-5 during storage, this should be watched carefully in the future. The increased use of hydrotreating to make JP-5 in the future is a possibility.
- (5) Carboxylic acids in JP-5 have been shown to be capable of attacking metals such as cooper, zinc, lead and cadmium.
- (6) Certain natural occurring oxygen compounds present in JP-5 are believed to have anti-oxidant characteristics. It is possible that severe hydrotreating can remove these oxygen compounds requiring the use of anti-oxidant additives.
- (7) Olefins are controlled by specifications to 5 vol % and in JP-5 currently being processed do not appear to present a problem. However, the possibility of having JP-5 made in the future from thermally cracked stocks would possibly increase the chances of thermal stability problems as a result of changed olefin compound types. Proper post hydrotreated should, however, minimize these effects. Thus, the trend in problem severity is designated PI, Potential to Increase.
- (8) Disulfides and polysulfides behave much like peroxide compounds and are thus potentially very deleterious to deposit formation. Though there is no apparent trend in the current levels of these compounds, they can be generated in certain mercaptan sweetening processes. Since there is a definite increasing trend in the sulfur compound levels of crudes being processed in the U.S. and abroad, there is a potential for greater use of mercaptan sweetening processes in JP-5 processing, particularly among small refineries that do not have hydrotreatment capabilities.
- (9) In connection with the above, the potential use of the copper chloride sweetening process, which forms soluble copper compounds should be watched. At the current time, however, this sweetening process is not employed in the making of JP-5.
- (10) The level of carboxylic acids are controlled indirectly by the acid number specification.

- (11) The peroxide buildup in certain JP-5 shipments which subsequently attacks a neoprene diaphragm in certain Navy planes has been studied and documented (NAPC-LR-78-20).
- (12) The increasing sulfur levels in the crudes being used in the U.S. and abroad may result in an increase in number and/or severity of hydrotreatment processes used to make JP-5.
- (13) The Air Force has experienced kerosine jet fuel thermal stability problems (in experimental fuels) which have been related to disulfides/polysulfides formed in the Doctor sweetening process.
- (14) Copper leaching into JP-5 has been a problem in the connection of the use of Admiralty metal alloy on aircraft carriers.

TABLE 37

PROBLEM ANALYSIS MATRIX - FUEL COMBUSTION

Covered By Mil. Spec	Yes	Yes	ON S	7 4 8 P 8	Yes	Yes .	113 S	Yes	o <sub>N</sub>	, ,	Yes	Yes
Particulate, Or Gaseous Emissions	χ(5)	(5) <sup>X</sup>	x(5) ,(5)	, , ,	0 0	(9) <sup>X</sup>	0	. 0	0(13)	c	<b>&gt;</b> 0	0
Trends In Problem Severity										<b>+</b>	NAT	NAT
Prfor Incidents, Problems	(9) <sup>X</sup>	(e) X	o >	0(14)		0	0	0(15)	0	c	0 0	0
Impact Sensitivity Of Engine/ Airframe	x(3)	(E) X	(e)*	; o	×	×	0	×	0	×	0	0
Storage and Handling	0	0	00	· ×	0	0	0	×	0	×	×	0
Ignition	0	0	0 0	×	x (11)	\ \ \ \ \ \ \ \ \ \	0	0	0	0	0	×
Fuel Processing	x(2)	X(2)	X(2) X(2)	x(8)	x(8) (10)	(S. ) X	X(12)	X (21)	6110	0	0 (	<b>5</b>
Crude 011 Type	E <sub>x</sub> E	; ;	(E) <b>x</b>	0(7)	(OL)*	X	o	X (13)	200	0	0 0	>
Fuel Components/ Properties Which Impact On Combustion	Smoke Point	Total Aromatics	Hydrogen Content	Flash Point	Distillation Curve	(1) conc.	Heat of Combustion	Total Sulfur	lotal Mitrogen	Additives Corrosion Inhibitor	Anti-Oxidant Anti-Irin	7) 

#### FOOTNOTE EXPLANATIONS FOR FUEL COMBUSTION MATRIX

- (1) Smoke point, total aromatics, polynuclear aromatics and fuel hydrogen content are all affected by the nature of the crude mix used.
- (2) The type of specific fuel processing scheme that is used to prepare the JP-5 can greatly affect the above fuel components/properties. Since there is a strong interaction between the nature of the crudes used and the type of processing employed, both aspects of the production of JP-5 must be considered in estimating the effect on combustion characteristics.
- (3) The formation of soot is greatly dependent on the hydrogen content of the fuel which can be related to total aromatics content and to a lesser extent to the types of aromatic compounds present. The degree of soot formation can affect turbine blade erosion combustor wall temperature, both of which can greatly affect engine life and maintenance requirements.
- (4) As a result of the use of higher aromatic content crudes, such as that obtained from the Alaskan North Slope, there will be increased pressure on smoke point aromatics, hydrogen content specifications and a greater degree or amount of downstream processing required to meet these specifications.
- (5) Generally, the higher the aromatics content of the fuel produced (lower the hydrogen content), the more prone it will be to produce carbon particulates. However, many other factors such as engine design and operating conditions will also have an important effect on the level of particulates. Also, fuel hydrogen content can affect gaseous pollutant emissions including carbon monoxide, hydrocarbons, and nitrogen oxides.
- (6) Variations in fuel viscosity could cause minor changes in fuel spray patterns which, in turn, could cause variations in the combustion processes. This could lead to changes in the formation of soot as well as other gaseous pollutants.
- (7) Within the limits of initial and final boiling points for the JP-5 specification, generally only minor differences in volatility distribution will be exhibited by a wide range of crudes.

  The flash point is primarily determined by the initial boiling point of the distillates and has been correlated well with distillates independent of the history of the crudes.

- (8) Flash point of JP-5 should not generally be affected by fuel processing. However, the distillation curve of a crude can be altered through the use of cracking reactions which reduce the molecular weight of higher boiling point components.
- (9) There is no apparent trend in the character of distillation curves of JP-5 currently being produced, though hydrocracking is now being used in one U.S. refinery for JP-5 production.
- (10) Only relatively minor changes are anticipated in JP-5 fuel viscosity as a function of crudes used or fuel processing employed.
- (11) Ignition characteristics can be affected by changes in resultant fuel viscosity (as it affects injector spray patterns). However, since only relatively minor changes are anticipated in fuel viscosity as a result of crude/processing interactions, this should not be a problem. One possible exception would be fuel derived from synthetic sources.
- (12) Fuel processing that can affect the hydrogen content of the fuel (hydrogenation, hydrocracking) or indirectly through selective aromatics extraction can result in small changes (e.g. 1-2%) in fuel heating value. Hydrogenation of distillates to aromatics decreases heating values on a mass basis, but there is also a concomitant increase in fuel density so that the net effect is generally a fuel with a higher heating value on a volume basis.
- (13) Nitrogen content of fuels that are currently derived from conventional petroleum sources does not present any major problems as far as fuel combustion is concerned. However, crudes that may be derived from shale in the future may have significantly higher nitrogen content which would have to be reduced by further downstream processing. Shale derived crudes could produce greater quantities of  $NO_x$  emissions.
- (14) Flash point is primarily a safety specification and, in this connection, there have been previous incidents that have been related to this property. It is listed among the components/ properties which impact on combustion in that it is closely controlled by the low end volatility portion of the fuel which also impacts on ignition characteristics.
- (15) Total sulfur is not generally considered a specification that impacts directly on the combustion of JP-5. However, the corrosion of turbine blades and other turbine parts are affected by the total sulfur content of the fuel as well as combustion temperature and engine environment.

## 7.3 Lubricity

The Matrix analysis for the fuel lubricity area is presented in Table 39. Footnote explanations to the Lubricity Matrix are given in Table 40.

The major points made by the Lubricity Matrix include the following:

- Mild hydrotreatment should not affect lubricity. However, use of severe hydrotreatment may produce fuels with poorer than average lubricity characteristics, depending upon the specific processing conditions employed as well as the crude (or crude mix) being processed. Since a trend is developing toward this end (to handle crudes of higher sulfur and aromatics content) it is anticipated that JP-5 jet fuel lubricity may become more of a potential problem area in the future.
- A corrosion inhibitor has been specified in the latest military specification for JP-5, primarily as a lubricity improver. The presence of corrosion inhibitors (generally formulations containing di-carboxylic acids with or without organic phosphates) may increase the tendency of the fuel to retain water and thus potentially cause problems with the WSIM specification. Also, the greater tendency of the fuel to retain water may indirectly cause lubricity problems through increased corrosion effects.
- Failures of the F-14-A afterburner hydraulic fuel pumps were traced to the use of low lubricity JP-5 fuel which, in turn, were linked to the use of severe hydrotreatment in the processing of certain batches of JP-5.
- The use of a hardware solution, i.e. changing or modifying a specific engine component, that may be particularly sensitive to changes in fuel lubricity may offer a more attractive approach than the use of additives such as corresion inhibitors, which can adversely affect other fuel properties.

#### 7.4 Low Temperature Flow Properties

The Matrix Analysis for JP-5 low temperature flow properties is shown in Table 42. Footnote explanations to this Matrix is presented in Table 43.

The major points made by the Low Temperature Flow Matrix include the following:

- The inherent composition of crudes will have the predominant effect on jet fuel composition as minimal use of conversion processes is currently used in making JP-5. However, as conversion processes become more widely used in the production of JP-5, the processing effect on fuel freeze point will become more pronounced. From a molecular standpoint, n-paraffins have the highest freeze point for a given molecular weight, and thus control the freezing characteristics of jet fuels. Aromatics have the lowest freeze point with naphthenes showing intermediate behavior.
- Current specification fuels derived from conversion processing such as hydrocracking may actually have improved low temperature flow properties as a result of conversion of high molecular weight n-paraffins to branched chain paraffins. However, use of broadened specification fuel would likely increase the low temperature flow problem.

- Shale derived fuels are high in n-paraffin content and thus may have more severe low temperature flow properties.
- Under most terrestrial storage conditions, low temperature flow properties of JP-5 are not a problem. However, for fuel handling and storage in certain extreme environments, such as the polar regions, fuel freeze point and low temperature flow of JP-5 could become an important consideration.
- Low temperature flow improver additives are not currently used in JP-5, though they have been used for many years to improve the low temperature properties of middle distillate heating oils and diesel fuels. The addition of these additives to a fuel dramatically changes the manner in which wax crystals grow. Thus, the use of wax crystal modifier additives specifically formulated for JP-5 use could be attractive in helping to improve low temperature flow properties.

TABLE 39

PROBLEM ANALYSIS MATRIX - FUEL LUBRICITY

Fuel Components/Properties Which Impact On Lubricity Problems	Crude 011 Type	Fuel Processing	Storage and Handling	Impact/ Sensitivity Of Engine/Airframe	Prior Incidents, Problems	Trends In Problem Severity	Covered By Mil. Spec
Total Aromatics	×	(L) <b>X</b>	0	×		(٤) <sup>I</sup>	Yes
Polynuclear Aromatics	×	(1) <sup>x</sup>	0	×		I(3)	No
Total Sulfur	×	×	0	0		I(3)	Yes
Heterocyclic Sulfur	×	×	0	×		I(3)	No
Total Polar Compounds	×	×	0(14)	0		Id	No O
Total Acidity	×	×	0	0		Id	Yes
Total Nitrogen	(21)0	(12) <sub>X</sub>	0	0		pI(12)	- 118 2
Heterocyclic Nitrogen	0(12)	x(12)	0	0		PI (12)	8 <b>-</b> &
Water Content	0	(11) <sup>X</sup>	×	×		NAT	N N
MSIM	0	×	×	×		$_{ m pl}^{(13)}$	Yes
Smoke Point	(6) <sup>X</sup>	(01) <sup>X</sup>	0	×		PI (3)	Yes
Hydrogen Content	(6) <sup>X</sup>	(L)×	0	×		pI (3)	ON.
Additives							
Corrosion Inhibitor	0	0(4)	x(5)	(9) <sup>X</sup>		(8) PI	Yes
Anti-Oxidant	0	0	0	0		0	Yes
Anti-Icing	0	0	0	0		0	Yes
Metal Deactivator	0	0	0	0		0	Option

# FOOTNOTE EXPLANATIONS FOR THE FUEL LUBRICITY MATRIX

- (1) High aromatic content crudes may receive more severe hydrotreatment in the production of JP-5. Increased severity of hydrotreatment may produce fuels with poorer than average lubricity characteristics depending upon the specific processing conditions employed as well as the crude mix being treated, (e.g. High Aromatics Content North Slope Crude may require more severe hydrotreatment). It is presumed that reduction in concentration of specific polynuclear hydrocarbons, particularly napthalene derivatives, as a result of hydrotreatment, contributes significantly to degradation of Jet fuel lubricity.
- (2) The Navy began to experience lubricity problems in the mid1970's when A7B operating in the Mediterranean experienced fuel
  control valve hang-ups which were traced to the use of low lubricity fuels.\* Subsequent to this, failures of F-14A afterburner
  hydraulic fuel pumps were also traced to the use of low lubricity
  fuel. These lubricity problems have been linked to the use of
  severe hydrotreatment in the processing of certain batches of
  JP-5.
- The trends in both crude and aromatics content and severity of hydrotreatment (as well as refineries employing hydrotreatment) are increasing and thus the potential for occurrence of lubricity problems in JP-5 associated with these trends may increase. The Navy has already recognized these trends and has modified the JP-5 Military Specification to include the mandatory inclusion of a corrosion inhibitor (MIL-T-5624L) May 18, 1979, which has been shown to enhance fuel lubricity properties (See notes 4-8). It should be mentioned that the inclusion of the corrosion inhibitor as in effect a lubricity improver has been accompanied by downgrading of the minimum WSIM specification to 70.
- (4) A corrosion inhibitor has been specified in the latest military specification revision for JP-5, primarily as a lubricity improver. The formulations used generally contain di-carboxylic acids. Some also contain organic phosphate compounds.
- (5,6) The presence of corrosion inhibitor additives increases the tendency of the fuel to retain water which in turn can have a deleterious effect on the lubricity of the system. These effects are quite complex and depend to a large degree on system metallurgy and component design.

<sup>\*</sup>Grabel, Lawrence, "Lubricity Characteristics of JP-5 Fuels", NAPC-LR-79-6, 1A, March 1979.

- (7) Recent use of corrosion inhibitors placed in certain JP-5 batches (which were suspected of having lubricity problems) resulted in the lifting of oxide scale from pipes which caused the plugging of filter-separators in equipment on board an aircraft carrier.
- (8) The decision to include the corrosion inhibitor in all JP-5 now produced may indirectly lead to increased lubricity problems from corrosive action (of increased emulsified water) on certain parts. Again, the degree to which this may occur is a function of component (e.g. fuel pump), design, metallurgy, as well as the atmosphere to which the component is exposed.
- (9) Severe hydrotreatment may be required with certain crudes (e.g. North Slope Crude) in order to meet the minimum Smoke Point specification. This, in turn, could adversely affect fuel lubricity by removal of certain aromatic and heterocyclic species that are known lubricity improvers.
- (10) Processing by severe hydrotreatment (hydrocracking, hydrogenation) or aromatics extraction to improve the smoke point may result in the production of jet fuels with relatively poor lubricity properties.
- (11) Water retained in JP-5 as a result of processing (e.g. treatment with caustic solutions) could enhance corrosion in fuel system components, depending on design, metallurgy. The corrosive effects, in turn, could have an adverse effect on system lubricity.
- (12) In general, JP-5 derived from conventional petroleum crude sources is not processed to remove nitrogen compounds (the levels being far below that which are of concern). However, the presence of some heterocycle nitrogen compounds, present in trace levels could affect fuel lubricity. Severe hydrotreatment to reduce aromatic levels (and/or meet fuel smoke point specification) could concomitantly remove trace heterocyclic nitrogen compounds.
- (13) The addition of the corrosion inhibitor to JP-5 as a means of minimizing fuel lubricity problems may result in a greater tendency for the fuel to retain water through emulsion formation. This, in turn, could have an adverse effect on corrosion and, long range, possibly on lubricity, if the metallurgy of key parts is affected.
- (14) Contamination of JP-5 in storage and transfer with polar compounds such as water can affect corrosion of fuel system parts which, in turn, could have adverse effects on system lubricity.

TABLE 41

PROBLEM ANALYSIS MATRIX - LOW TEMPERATURE FLOW PROPERTIES

Covered By Mil. Spec.	0 0 0 0 0 0 0	Yes Yes Yes	Yes No No No	Yes
Trends In Problem Severity	$\begin{array}{c} \text{NAT} \\ \text{NAT} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} (9)$	NAT NAT	NAT NAT NAT	NAT (11)
Prior Incidents Problems				
Impact/ Sensitivity of Engine/Airframe	(3) (3) (3) (3) (3) (3) (4) (4) (4) (4) (4) (4) (4) (4) (4) (4	(8) (8) (8) (8)	<u>88888</u> ****	(11) <sub>X</sub>
Storage and Handling	0000	000	00(2)	(11) <sub>X</sub> (10) <sub>X</sub>
Fuel Processing	X X X X X X (2)	X (5) X (5) X (5)	(2) (2) (2) (3) (4) (4) (4) (4) (4) (4) (4) (4) (4) (4	(11) <sub>X</sub> (01) <sub>X</sub>
Crude Oil Type		*** 444 (4)	**** 44440 6	0 (01) <sup>X</sup>
Fuel Components Which Impact On Freeze Point/ Low Temperature Flow	n-Paraffins Isoparaffins Naphthenes Aromatics	Distillation Curve 90% Recovered End Point	Freeze Point Viscosity at (-20°C) Cloud Point Pour Point Viscosity/Temperature Relationship	Additives Anti-Icing Pour Depressants/ Flow Improvers

# FOOTNOTE EXPLANATIONS FOR LOW TEMPERATURE FLOW PROPERTIES MATRIX

- (1) The inherent composition of crudes will have the predominant effect on jet fuel composition as minimal use of conversion processes (e.g. hydrocracking catalytic cracking) is currently used to make JP-5. From a molecular standpoint, molecular symmetry and isomeric effects can have an important impact on jet fuel freeze point, i.e. for a given molecular weight, freezing point (of pure components) generally is controlled by concentrations of large molecular weight n-paraffins which have the highest freeze point. Also, highly symmetrical branched isomers may have very high freezing points. In general, the greater the degree of asymmetrical branching of the paraffin molecules, the lower will be the jet fuel freeze point.
- (2) Current processing technology provides the potential to alter the relative amounts of n-paraffins, isoparaffins, naphthenes and aromatics that are present in the crude oils used. Long chain n-paraffins, considered most important in controlling the freeze point of jet fuels, can be removed by the use of selective molecular sieve adsorption processes or selective hydrocracking. Also, greater branching can be affected by cracking and isomerization processes.
- (3) The molecular weight distribution as well as relative concentrations of the types of compounds listed will affect the low temperature limit of operability of the aircraft as it impacts on freezing point.
- (4) The heavy ends, or highest molecular weight components control the freeze point of the fuels. Levels of these compounds can be related to the low volatility portion of the distillation curve.
- (5) Fuel processing as indicated above in (2) can affect these low temperature flow properties.
- (6) Viscosity/temperature coefficients can be affected by the relative amounts of n-paraffins, aromatics and alicylic compounds. In general, however, the differences in composition of the various sources of JP-5 are such that large differences in viscosity-temperature coefficient are ususally not observed.
- (7) Under most terrestrial storage conditions, low temperature flow properties are not a problem. However, for the cases of fuel handling and storage in certain extreme environments such as the polar regions, fuel freeze and low temperature flow properties could be a factor. Prolonged flight in cold environments can also create problems with wax formation in wing tanks.
- (8) The distillation curve, 90% distilled points and end points, are also a measure of fuel volatility and thus can impact on engine ignition characteristics.

- (9) The trend is clearly toward higher aromatics levels in the crudes being used to make JP-5. As a class of compounds, aromatics have the lowest freeze point (for a given molecular weight); however, the jet fuel freeze point and low temperature flow properties are controlled, in practice, by the levels of relatively high molecular weight n-paraffins present.
- (10) Low temperature flow improver additives are not currently used in JP-5, though they have been used for many years to improve the low temperature properties of middle distillate heating oils and diesel fuels. The addition of these additives to a fuel dramatically changes the manner in which wax crystals grow. Thus, the use of wax crystal modifier additives specifically formulated for JP-5 use could be attractive in helping to improve low temperature flow properties.
- (11) Anti-icing additives are placed in JP-5 to prevent the freezing of any water that has accumulated in the fuel. Its effect on the hydrocarbon components of the fuel is negligible.

### 7.5 Additive Effects and Interactions

There are three additives currently being used in JP-5 fuel. They include:

- Anti-Icing Agent Ethylene glycol monomethyl ether (EGME) (prevents freezing of trace water in the fuel)
- Corrosion Inhibitor Blends of dicarboxylic acids (placed in the fuel to improve lubricity characteristics)
- Anti-Oxidants Usually blends of phenols (placed in the fuel to prevent buildup of peroxides).

Each of the above additives has a specific function as indicated. However, there are several additive side effects and some interactions that have potential significance to the current and future performance of JP-5. Thus, a Matrix summarizing Additive Effects and Interactions was prepared and is presented in Table 43. Footnote explanations to this Matrix are given in Table 44.

The major points made in the JP-5 Additives Interactions Matrix include:

- The anti-icing additive EGME depresses the flash point of the distillate for JP-5 by about 6°F. Evidence for this estimate is presented in Appendix A. A new additive, diethylene glycol monomethyl ether (DEGME) which does not reduce the flash point of JP-5 is currently being tested.
- A corrosion inhibitor was recently put in JP-5 to improve fuel lubricity characteristics. However, use of this additive has required that the WSIM specification be downgraded as the additive may make the fuel more susceptible to increased water retention. Thus, a greater burden may now be placed on filter-separator equipment as a result of the use of corrosion inhibitors.
- Anti-oxidants are used to prevent the formation of peroxide compounds which can lead to deposit formation. Previously required only for hydrotreated fuels, these additives are now mandatory for all JP-5 produced.
- Metal deactivators can remove dissolved copper from JP-5 which in turn could improve thermal and storage stability as dissolved copper has been known to catalyze the oxidation of hydrocarbons. Metal deactivators can be used at the option of JP-5 suppliers. However, they are rarely employed in JP-5.

TABLE 43

The second secon

PROBLEM ANALYSIS MATRIX - ADDITIVE EFFECTS AND INTERACTIONS

FUEL PERFORMANCE/PROPERTIES AFFECTED BY ADDITIVES

(Ss.	Lubricity X(5) 0 x(15) 0 0	Combustion X(1) X (1) 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	Thermal Stability 0 0 0 (8) x (12) 0 0	Temperature Flow (2) (2) (14) (14)	Availability X(3) 0 0 0 0	Storage/ Handling X(6) X(9) X(14) X(12) X(13) X(13)	Anticipated Changes Changes Yes (4) Yes (10) Yes (10) No No No
Corrosion inhibitor/ Anti-Oxidant Corrosion Inhibitor/ Anti-Static	(LL)X	<b>5</b> 0	<b>.</b> 0	o 0	o o	(11) <sup>X</sup>	

(\*) Not currently used in JP-5.

#### FOOTNOTE EXPLANATIONS TO ADDITIVES EFFECTS AND INTERACTION MATRIX

- (1) The current anti-icing additive used in JP-5, ethylene glycol monomethyl ether (EGME) has a high volatility and actually decreases the flash point of the distillate for JP-5 by about 6°F. Since the low end volatility of the fuel is increased, it is possible that fuel ignition characteristics could be affected but these effects should be relatively minor.
- (2) The anti-icing additive prevents freezing of entrained and/or dissolved water and to this extent has a beneficial effect on fuel low temperature flow.
- (3) The current anti-icing additive ethylene glycol monomethyl ether reduces the flash point of JP-5. As a result, a somewhat narrower distillate cut must be used to meet the flash point specification. This significantly reduces the potential JP-5 availability.
- (4) The Navy has been field testing a new anti-icing additive diethylene glycol-monomethyl ether (DEGME) to replace the existing EGME (99,100). This new additive would not degrade the fuel flash point.
- (5) The corrosion inhibitors recently put in JP-5 have a significant effect on improving fuel lubricity characteristics. However, use of these additives is accompanied by a down rating of the WSIM specification, and may put a greater burden on filter separators.
- (6) The use of a corrosion inhibitor may cause some lifting of scale in storage tanks and/or greater emulsification tendency of the fuels. This, in turn. could lead to plugging of filter separators. Some problems with filter separator failure have already been experienced by Navy personnel.
- (7) Use of a corrosion inhibitor, typically dicarboxylic acid (some formulation also contain organic phosphates) has recently been made mandatory.
- (8) (9) (10) Anti-oxidant additives are used to prevent the formation of peroxide compounds which can lead to sediment formation in storage, and at higher temperatures deposit formation in the engine. Anti-oxidant additives are now mandatory in all JP-5 produced, without regard for the type of processing used. Previously, it had only been required where hydrotreating was used in processing the fuel.
  - (11) Some evidence exists that the presence of some anti-oxidant additives in JP-5 will further increase the WSIM degradation effect of corrosion inhibitors. As indicated above, this could lead to increased water retention, corrosion, and/or plugging of filter separators.

- (12) Metal deactivators can remove dissolved copper from JP-5 which in turn could, thus, improve thermal and storage stability as copper has been known to catalyze oxidation of hydrocarbons. Metal deactivators can be used at the option of the supplier. However, they are rarely employed for JP-5.
- (13) Anti-static, conductivity improvers can also enhance the WSIM degradation effect of corrosion inhibitors. Anti-static additives are not currently used in JP-5.
- (14) Low temperature flow improvers for distillate fuels are typically low molecular weight polymers which modify wax crystallization. They can thus improve both low temperature pumpability and storage characteristics of JP-5. However, this type of additive is not currently used in jet fuels.

### 8. TASK 10 FINAL ASSESSMENT OF PROBLEM AREAS

As a result of the work conducted during this program, several potential problem areas have been identified concerning the quality/performance and availability of JP-5 produced in the present and near future. Several of these have been assessed as to their effect on the major technical areas having an impact on JP-5 quality in the Matrix Check lists presented in Task 9. A brief review and discussion are presented below on each of the potential problem areas that could have an important impact on the quality/performance and potential availability of JP-5 produced in the near future.

### 8.1 Fuel Quality/Performance

There is a trend toward the use of poorer quality crude oils in the U.S. as the availability of light, sweet crudes become increasingly tight. The lower quality is reflected primarily in the increased levels of total sulfur, mercaptans, aromatics content as well as in a smaller fraction of middle distillate available for making JP-5. This trend is particularly important in PAD 5 where many larger refineries are using increasing quantities of North Slope Alaskan Crude which is relatively high in aromatics and sulfur compounds.

The immediate effect of the above trend, is to create greater difficulty in meeting the Smoke Point and Total Aromatics specifications for JP-5. This is particularly the case for the very small refineries that have limited aromatics removal capacity (either hydrotreatment or extraction/separations processing).

Other indirect effects of decreased crude quality are also beginning to take place. The use of increased severity hydroprocessing (in an attempt to reduce sulfur and/or aromatics levels) can result in the production of JP-5, which has poorer lubricity characteristics and/or poorer thermal stability characteristics. Both arise from the fact that severe hydrotreatment can affect the removal of trace impurities that can act as lubricity promoting agents and/or anti-oxidants.

Several chemical processes used in the production of JP-5 can produce some side effect processing problems and must be used with care. Oxidative Sweetening processes produce disulfide compounds which behave much like peroxide compounds and can adversely affect thermal stability. Caustic washing can produce disulfide formation and also increase the tendency of the fuel to retain water, thereby potentially causing some problems with the WSIM specification.

Many small refineries in PAD 5 have limited processing capability and thus have little flexibility in the type of crudes they can process. In general, Smoke Point, WSIM and Freeze Point are the specifications that small refiners have most difficulty in meeting.

The use of additives such as anti-icing agents, and corrosion inhibitors can have a dramatic effect on fuel properties and performance. Extreme care must be exercised when a new additive is put in the fuel or when a change in additive concentration is made. Though such changes may be used to mitigate a particular problem, they may intensify or promote another. A good example is the addition of a corrosion inhibitor to improve fuel lubricity. Such a change could cause increased difficulty with the WSIM specification, which in turn could cause other operating problems associated with increased water content in the fuel.

Based on the above discussions and the work conducted in the previous tasks, the following assessment is made regarding the major problem areas affecting fuel quality and/or performance.

## Fuel Storage/Thermal Stability

- Increased use of a more severe hydrotreatment (to handle lower quality crudes) may make JP-5 produced in the future more susceptible to peroxidation due to the potential greater removal of natural antioxidants. The use of anti-oxidant additives should, however, continue to offer a viable approach to minimize this problem.
- The possible use of thermally cracked stocks to make JP-5 in the future may lead to the formation of a wider range of olefin compound types which could result in increased susceptibility to thermal degradation. However, the use of the proper hydrotreatment technology applied to thermally cracked stocks can prevent such effects.
- Use of Oxidative Sweetening processes which form disulfides should be minimized where possible in the production of JP-5 as these compounds behave much like peroxides in chemical reactions.

#### Fuel Combustion

• Overall, Total Aromatics content should increase toward the acceptable specification limit as a result of the use of lower quality crudes. This will place an increased burden on some combustor components if higher combustion temperatures result from soot radiation. This trend could be offset by a greater use of hydrogenation or hydrocracking in the processing of JP-5 (see below).

#### Lubricity

- Increased use of severe hydrotreatment to handle lower quality crudes (e.g. hydrogenation, hydrocracking) may lead to some degradation in fuel lubricity characteristics.
- The use of a hardware solution, i.e. changing or modifying a specific engine component, that may be particularly sensitive to changes in fuel lubricity may offer a more attractive approach than the use of additives such as a corrosion inhibitor, which can adversely affect other fuel properties.

### Low Temperature Flow Properties

• In the near term, the inherent composition of the crudes used to make JP-5 will have the predominant effect on jet fuel composition as minimal use of conversion processing is currently used in the production of JP-5. Trends toward the use of crudes with higher aromatics content and relatively lower levels of n-paraffins may actually reduce JP-5 freeze point problems if current specifications are maintained. Furthermore, the use of conversion processes such as hydrocracking, that reduce the molecular weight of higher n-paraffins, converting them to smaller branched chain molecules, will also tend to facilitate meeting the JP-5 freeze point specification. However, the broadening of current specifications of JP-5 to help increase supplies would tend to intensify the low temperature flow problem.

### Additive Effects/Interactions

- Extreme care must be exercised in prescribing the use of additives to solve a particular fuel problem as they often can create another problem. Examples pertinent to JP-5 include -
  - + Use of anti-icing additive ethylene glycol monomethyl ether which depresses the Flash Point about  $6^{0}F$ , and in turn results in a reduced yield of middle distillate for JP-5.
  - + The use of a corrosion inhibitor to improve fuel lubricity characteristics which can have an adverse affect on WSIM.

#### 8.2 Fuel Potential Availability

The future potential availability of JP-5 is a function of several factors, many of which are difficult to assess. They include -

- General availability of crude oil to U.S. and foreign refineries. This factor is subject to international events and thus can be quite unpredictable. Severe shortages in overall crude supply can result if the source of supplies from any or all of the major countries supplying the U.S. were temporarily cut off. The degree to which crude embargoes could impact on JP-5 supplies would, in turn, depend on many factors, but in times of national emergency, production of military fuels will have a very high priority.
- Overall Quality (Yield) of Crude. The overall average yield of distillate within the current Freeze Point/Flash Point specification limits will determine the maximum theoretical yield of JP-5 that can be obtained without the use of conversion processing. The general trend here is toward heavier crudes which should reduce the potential maximum theoretical yield of JP-5 available by distillation.

- Availability and Use of Conversion Processing. The use of conversion processing [e.g. hydrocracking catalytic or thermal cracking + hydrogenation has the potential to expand overall middle distillate supplies in a trade-off with reduced use of heavier feedstocks or competitive products (gasoline)]. Thus, the extent to which these processes are used in the future and their general availability in refineries will have a definite impact on potential JP-5 supplies. Most refinery projections show modest near-term growth of refinery conversion processing capability. This should help potential JP-5 availability.
- Number of Refineries Participating In JP-5 Contracts. Currently there is only about 13% of U.S. refinery capacity participating in the production of JP-5. Thus the expansion of the base of participating JP-5 refineries in the U.S. (as well as foreign refineries) offers a large potential to increase JP-5 supplies.
- The Competitive Demand For Other Fuels. There is considerable uncertainty in the projections of demand for fuels that compete with JP-5. However, most published projections look for an increase in the competitive demand for other middle distillates. This should come primarily from a gradual conversion of the U.S. fleet of automobiles and trucks to the use of diesel engines and thus increased demand for diesel fuel. In addition, most projections on the demand for commercial jet fuel show a small growth increase in the near future which should put increased pressure on the demand for middle distillates.

On the other hand, the projected reduced use of gasoline may make heavier stocks and some conversion processing facilities such as hydrocracking, catalytic cracking (previously used to make gasoline) more readily available to make middle distillates which could counteract the above effects somewhat. Also, if coal is substituted to a greater extent in applications where heavy residual oil is currently being used, more residua may be made available for increased middle distillate supplies through conversion processing.

Much of the above is uncertain, but the extent to which more conversion processing is employed to make JP-5 as well as other middle distillates will have a favorable effect on potential JP-5 supplies, though it will require some additional incremental cost above conventional processing. Also, overall directions in the state of the economy will have an important impact on the above.

#### 9. REFERENCES

- 1. Capability of U.S. Refineries to Process Sweet/Sour Crude Oil, March 15, 1978, National Petroleum Refiners Association.
- 2. Hydrocarbon Process 57 #5:19 (May, 1978).
- 3. Wall Street Journal, October 26, 1977.
- 4. Oil & Gas Journal, p. 43, May 1, 1978.
- 5. Oil & Gas Journal, p. 26, May 1, 1978.
- 6. Oil & Gas Journal, p. 21, May 29, 1978.
- 7. Oil & Gas Journal, p. 26, May 23, 1977.
- 8. Private Communication, Robert Lynch, Defense Fuel Supply Center, Technical Operations Directorate.
- 9. Oil & Gas Journal, p. 108, March 20, 1978.
- 10. Oil & Gas Journal, p. 148, December 26, 1977.
- 11. Oil & Gas Journal, p. 63, March 20, 1978.
- 12. Private Communication, D. Calhoun, Defense Fuel Supply Center Procurement Directorate.
- Wall Street Journal, October 19, 1978.
- 14. Oil and Gas Journal, September 11, 1978, p. 58.
- 15. Oil and Gas Journal, September 25, 1978, p. 107.
- 16. Oil and Gas Journal, October 9, 1978, p. 30.
- 17. Chemical Engineering, <u>85</u> # 17:35, (7/31/78).
- 18. Chemical Engineering, 85 #13:94, (6/5/78).
- 19. Wall Street Journal, July 26, 1978.
- 20. Hydrocarbon Processing, August 1978, p. 13.
- 21. Private Communication with DOE Officials, November 3, 1978.
- 22. Petroleum Import Data Handbook, 1977 Edition, John G. Yeager and Associates, Inc., Oxford Petroleum, Inc., Houston, Texas.
- 23. Oil and Gas Journal, August 8, 1977, p. 38.

- 24. Hydrocarbon Processing 1978, "Refinery Handbook Issue" September, 1978.
- 25. 011 and Gas Journal, October 23, 1978, p. 131.
- 26. 011 and Gas Journal, October 23, 1978, p. 207.
- 27. Erdoel, Erdgas Z, 94 # 3:67 (March, 1978).
- 28. Oil and Gas Journal, October 16, 1978, p. 33.
- 29. Wall Street Journal, October 10, 1978, p. 2.
- 30. Oil and Gas Journal, October 2, 1978.
- 31. Dukek, W. G., "Refining Jet Fuel for Thermal Stability", paper presented at the "Jet Fuel Thermal Stability Workshop" Nasa-Lewis Research Center, Cleveland, Ohio, October 27, 1978. (See Appendix III)
- 32. Taylor, W. F., "Development of High Stability Fuel" Contract N00019-71-C-0463, Final Report, April, 1972.
- 33. Hydrocarbon Processing, <u>52</u>, 1973, p. 69-74.
- 34. Modern Petroleum Technology, Institute of Petroleum, 1962.
- 35. Hydrocarbon Processing, p. 19, February, 1978.
- 36. National Petroleum News, July, 1978.
- 37. Hydrocarbon Processing, p. 15, December, 1977.
- 38. Oil and Gas Journal, p. 51, November 6, 1978.
- 39. Oil and Gas Journal, p. 42, July 3, 1978.
- 40. Oil and Gas Journal, p. 85, Vol. 78, September 18, 1978.
- 41. Hydrocarbon Processing, p. 113 and 122, May, 1978.
- 42. Chen, N. Y. and Garwood, W. E., "Selective Hydrocracking of n-Paraffins in Jet Fuels" Industrial Engineering Chemistry Process Design and Development, Vol. 17, No. 4, p. 513, 1978.
- 43. Oil and Gas Journal, p. 76, October 2, 1978.
- 44. 011 and Gas Journal, p. 34, February 13, 1978.
- 45. Wall Street Journal, November 17, 1978.
- 46. Small Refiner Bias Analysis Final Report, January, 1978, HCP/B7025801.

- 47. Wall Street Journal, November 22, 1978.
- 48. New York Times, November 22, 1978.
- 49. Monthly Report No. 1, August October, 1978.
- 50. Oil and Gas Journal, p. 116, November 13, 1978.
- 51. Monthly Report No. 2, October November, 1978.
- 52. Wall Street Journal, October 17, 1978.
- 53. Wall Street Journal, October 12, 1978.
- 54. Platt's News Service, October 6, 1978.
- 55. Oil and Gas Journal, August 7, 1978.
- 56. Holder, G. A., and Winkler, J., "Wax Crystallization From Distillate Fuels" J. Institute of Petroleum, <u>51</u>, #499 (1965).
- 57. Chemical Engineering Progress, p. 67, December 1978.
- 58. Hydrocarbon Processing, p. 117, May 1978.
- 59. New York Times, December 14, 1978.
- 60. Gantt, J. E., Chemical Engineering Progress, p. 69, December 1978.
- 61. Wall Street Journal, December 13, 1978.
- 62. Oil and Gas Journal, p. 72, December 25, 1978.
- 63. Wall Street Journal, December 11, 1978.
- 64. Oil and Gas Journal, p. 31, July 10, 1978.
- 65. 011 and Gas Journal, p. 45, November 27, 1978.
- 66. Oil and Gas Journal, p. 24, December 18, 1978.
- 67. Findings and Views Concerning the Exemption of Kerojet Fuels From the Mandatory Petroleum Allocation and Price Regulation, DOE/ERA-0001.
- 68. Wall Street Journal, January 11, 1979.
- 69. Wall Street Journal, November 15, 1978.
- 70. 011 and Gas Journal, p. 36, December 18, 1978.

- 71. Oil and Gas Journal, p. 42, December 11, 1978.
- 72. Petroleum Economist, p. 521, December, 1978.
- 73. Petroleum Economist, p. 527, December, 1978.
- 74. Hydrocarbon Processing, p. 189, November, 1978.
- 75. Wall Street Journal, p. 3, February 5, 1978.
- 76. Anderson, C. J., "Alternative Fuels for Transportation: Implications of the Broad Cut Option" Lawrence Livermore Laboratory for ERDA W-7405-Eng-48, July, 1977.
- 77. "Aircraft Systems Fleet Support/Organic Peroxides in JP-5 Investigation" Final Report, NAPC-LR-78-20, September 27, 1978.
- 78. "Lubricity Characteristics of JP-5 Fuels" Interim Peport NAPC-LR -79-6 March 14, 1979.
- 79. Oil and Gas Journal, February 19, 1979.
- 80. W. F. Taylor and J. W. Frankenfeld "Development of High Stability Fuel", Final Report for Phase I Naval Air Propulsion Test Center, Contract N00140-74-C-0618, January, 1975.
- 81. K. Owen, Ch. 11 in "Modern Petroleum Technology", Inst. of Petroleum, London (1962).
- 82. V. A. Kalichevsky and B. A. Stagner "Chemical Refining of Petroleum", Reinhold, New York (1942) Chapter II.
- 83. K. Ownes in "Modern Petroleum Technology", 3rd Ed., Chapter 11, The Institute of Petroleum, London, 1962.
- 84. Hydrocarbon Processing, September, 1972, p. 216.
- 85. H. Kawahami and K. Hanano, Sekiyu Gakkai Shi, <u>15</u>, No. 9, 763 to 969 (1972).
- 86. K. M. Brown, Hydrocarbon Processing, <u>52</u>, 69 to 74 (1973).
- 87. A. C. Nixon, "Autoxidation and Antioxidants of Petroleum", Ch. 17 in "Autoxidation and Antioxidants", Vol. II, W. O. Lundberg, ed., Interscience, New York (1962).
- 88. J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry", W. A. Benjamin, Inc. (1964).
- 89. K. M. Brown, Hydrocarbon Processing, <u>52</u>, 69 (1973).

- 90. W. F. Taylor and J. W. Frankenfeld "Development of High Stability Fuel", Final Report for Phase III, Contract N00140-74-C-0618, Naval Air Propulsion Test Center (1976).
- 91. J. W. Frankenfeld and W. F. Taylor, "Alternate Fuels Nitrogen Chemistry", Final Technical Report for Contract N00019-76-C-0675, Naval Air Systems Command (1977).
- 92. W. F. Bland and R. L. Davidson, eds., Petroleum Processing Handbook, McGraw Hill, New York (1967).
- 93. Anon., Modern Petroleum Technology, 3rd Ed., Inst. of Petroleum, London (1962).
- 94. R. A. Jones, "Molecular Sieves", Ch. 3 in Vol. IV, Advances in Modern Petroleum Chemistry and Refining, S. J. McKetta, Jr., Ed., Interscience, New York (1961).
- R. H. Shertzer, "Aircraft Systems Fleet Support/Organic Peroxides in JP-5 Investigation", NAPC-LR-78-20, Final Report September 27, 1978.
- 96. L. Grabel, "Lubricity Characteristics of JP-5 Fuels", NAPC-LR-79-6, 1A, March 1979.
- 97. NAPC, Memo 10340 Ser. F1014.
- 98. R. N. Hazlett, et al, NRL Technical Memo, May 17, 1979.
- 99. L. Grabel, "Development of JP-5 Icing Inhibitor and Biocide Additive Package", NAPC-LR-78-23.
- 100. L. Grabel, Naval Air Propulsion Center, Private Communication.

# APPENDIX A

SUPPLEMENTARY TASK ON JP-5 SPECIFICATION SHEET ANALYSIS

### SUPPLEMENTARY TASK ON JP-5 SPECIFICATION SHEET ANALYSIS

JP-5 Specification Sheets from several U.S. refineries were obtained from the Navy Petroleum Office, Cameron Station, Virginia. It was felt that an analysis of these specification sheets might provide useful insight about potential problem areas that might arise in JP-5 production. Data from these sheets, which cover the time frame 1975-1978, have been reviewed and analyzed for possible trends, significant differences in properties and for consistency or variability. These data are summarized in Table 23.

Several inferences can be made from the data presented in Table 23. However, it is to be emphasized that these are inferences that are suggested by the data (whose reliability cannot be verified) and should not be considered as conclusive. Pertinent observations/inferences made from the specification sheet data are summarized below.

 Repeatability on Precision of Most Measured Specification Parameters is Good

Virtually all the tabulated specification parameters showed good repeatability with the precision being 10% or better for WSIM, Freezing Point, Flash Point and Smoke Point. Precision of the aromatics data markedly exceeded 10% in only one large PAD5 refinery. Precision of the total sulfur level parameter is much poorer than all the others ranging up to 100% for a few refineries. However, this does not present any problems as the absolute average level of sulfur for all the refineries investigated was generally more than 500% below specification levels.

• Some Parameters Are Operating Very Close to Specification Limits

For several of the refineries reviewed, the Flash Point (projected with anti-icing additive) and Smoke Point was operating very close to the JP-5 specification limits. In a few refineries, the % deviation of the test data for these parameters were very close to the average % deviation from the specification limit and thus even potentially able to exceed these limits causing rejection of that sample of JP-5. As shown below, the anti-icing additive ethylene glycol monomethyl ether depresses the Flash Point an average of about 6.30F after addition to the JP-5.

## Severe Hydroprocessing

Severe Hydroprocessing (large refineries V-D & V-G) produce JP-5 with very low aromatics and high smoke point. (Note the same result can be achieved without resorting to severe hydrofining if the crude mix is carefully controlled.)

TABLE A-1

SUMMARY OF JP-5 SPECIFICATION SHEETS FROM SOME U.S. REFINERIES

Spec	Refinery Code	General Processing Description	MSIM	F.P.°C	F1.P.ºF*	Aromatics	Sm.Pt.	Sulfur Wt %
Mean % Dev. % of Spec.	I-A	Small refinery, mild hydroprocessing	89.6 3.7%	-54 6.4% 9.8%	149.6 1.5% 1.1%	20.6 5.8% 21.45%		0.12
Mean % Dev. % of Spec.	V-C	Small refinery, clay filtration	0,	-51.8 2% 12.6%	142.2 1.0% 1.57%	22.4 8.3% 11.6%		0.033 33% 1112%
Mean % Dev. % of Spec.	H- V	Small refinery, mild hydroprocessing	d 97.3 2.7% 14.5%	.49.6 7.8%	151.0 1.1% 2%	21.3 7.0% 17.4%		0.063 51.4% 535%
Mean % Dev. % of Spec.	V-A	Small refinery, mild hydroprocessing		-49.3 7.8%	149.9 1.1% 1.3%	21.1 7.1%	19.5 1.3% 2.6%	0.066 70.3% 506%
Mean % Dev. % of Spec.	7-E	Large refinery, mild hydroprocessing	d 90.8 3.2% 6.8%	2.7% 20.9%	154.0 4.8% 4.1%	18.8 5.3% 33%	19.4 2.5%	0.033 52.5% 1112%
Mean % Dev. % of Spec.	V-D	Large refinery, sev hydroprocessing (Hydrogenation)	severe 97.6 1.5% 14.8%	-47.2 1.7% 2.6%	153 1.9% 5.4%	15.0 14.8% 66%	23.6 3.1% 24%	Nil
Mean % Dev. % of Spec.	9- <b>/</b>	Large refinery, severe hydroprocessing (Hydrocracking)	ere 93.1 3.8% 9.5%	-49.2 5.6% 6.9%	147.8 2.6% 5.6%	13.7 24% 83%	25.4 7.5% 33.6%	0.043 102% 830%
Mean % Dev. % of Spec.	0-111	<b>Large refinery,</b> caustic wash	93.1	-49.2 3.6% 6.9%	149 1.3% 6.4%	14.8 10% 69%	25.0 10% 32%	0.056 21.5% 1076%
Mean % Dev. % of Spec.	8-111	Large refinery, mild hydrofining		-48.8 2% 6%	144.4 2% 2.9%	18.1 6.7% 38%	21.1	0.034 37.4% 1076%
Mean % Dev. % of Spec.	111-C	Large refinery, Bender sweetening	der 94.6 3.1% 11.3%	-48.3 2.8% 5%	145.2 2.2% 3.7%	19.6 3.9% 27.9%	19.6 3.6% 3.2%	0.132 22.8% 203%
Mean % Dev. % of Spec.	A-111	Large refinery, mol. sieve paraffin removal mild hydrofining	. 99.2 val 1.6% 16.7%	2.5% 3.8%	148.6 3.6% 6.1%	20.6 8.1% 21.3%	20.3 3.3% 6.8%	0.016 67% 2400%

<sup>\*</sup> Without anti-icing additive.

 Effect of Anti-Icing Additive on Flash Point of Distillate Used to Make JP-5

The anti-icing additive ethylene glycol monomethyl ether, required in all JP-5 prepared in the U.S. and overseas, depresses the Flash Point of the distillate stock used to make JP-5 about 6-70F. The result of this anti-icing additive effect is to reduce the allowable volume available to make JP-5 in all crudes. The extent to which this reduction in distillate availability will take place will vary from crude to crude but can be significant as shown in Task 4. The data used to make this assessment were obtained from the JP-5 specification sheets of a major refinery in PAD3. They are summarized in Table 24.

The incentive is clearly apparent for finding an alternate, lower volatility anti-icing additive which will not lower the distillate Flash Point. Such an additive, diethylene glycol monomethyl ether, has recently been accepted for use in JP-5.

TABLE A2

ETHYLENE GLYCOL MONOMETHYL ETHER ANTI-ICING ADDITIVE DEPRESSES FLASH POINT OF JP-5 (1)

Flash Point Before Additive Addition, °F	Flash Point After Additive Addition, °F	Δ Flash Point, °F
156	146	10
156	148	8
154	148	6
154	150	4
154	150	4
156	150	6
152	146	6
154	150	4
158	150	8
154.9 (Mean)	148.6 (Mean)	6.3°F (Mean)

<sup>(1)</sup> Data obtained from Single Refinery over three year period.

